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Vertical transport rates in the stratosphere in 1993 from observations of CO_2, N_2O and CH_4.

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Abstract. Measurements of CO_2, N_2O and CH_4 are analyzed to define hemispheric average vertical exchange rates in the lower stratosphere from November 1992 to October 1993. Effective vertical diffusion coefficients were small in summer, ≤ 1 m^2s^{-1} at altitudes below 25 km; values were similar near the tropopause in winter, but increased markedly with altitude. The analysis suggests possibly longer residence times for exhaust from stratospheric aircraft, and more efficient transport from 20 km to the middle stratosphere, than predicted by many current models. Seasonally-resolved measurements of stratospheric CO_2 and N_2O provide significant new constraints on rates for global-scale vertical transport.

Introduction

Future high speed civil transports (HSCTs) are expected to inject H_2O and nitrogen oxides into the stratosphere. The residence time for the exhaust in the stratosphere will determine the magnitude of the associated perturbation to atmospheric chemistry. Residence times for stratospheric gases are currently estimated using observations of radioactive and volcanic debris, mostly in particulate form. These data reflect stratospheric transport rates only for particular single-point injections in the past.

To predict the impact of HSCTs, we must understand rates for meridional dispersion and vertical transport of exhaust continuously emitted over the globe. Boering et al. [*this issue*] documented the propagation through the stratosphere of seasonal cycles and long-term trends in tropospheric CO_2 [Keeling et al., 1989; Conway et al.,1988], relative to N_2O. Here we use data for N_2O, CO_2, and CH_4 obtained from the ER-2 during SPADE to derive seasonally-resolved rates for vertical exchange in 1992-93, averaged over midlatitudes in the Northern hemisphere stratosphere, and we discuss implications for predicted impacts of HSCTs.

Conceptual framework

Concentrations of stratospheric trace gases fluctuate with latitude, altitude, and time. However, variations for long-lived species are usually correlated [Ehhalt et al., 1983]: scatterplots of one tracer concentration against another give compact curvilinear relationships, often uniform on global scales [e.g., Fahey et al., 1990]. Plumb and Ko [1992] argued that compact global relationships arise by advection of trace species in the global residual circulation, modified by quasi-isentropic mixing by planetary-scale waves that propagate from the troposphere in winter [cf. Holton, 1986, Mahlman et al., 1986; Plumb and Mahlman, 1987; Schoeberl and Hartmann, 1991]. If quasi-isentropic mixing were much faster than non-conservative processes, isopleths for long-lived tracers would be parallel and transport of one tracer relative to another could be represented as a flux (F_{Z^*}) in one dimension, normal to the isopleths,

$$F_{Z^*} = -K(Z^*)\frac{d\sigma}{dZ^*}, \quad \text{where} \tag{1a}$$

$$K(Z^*) = \left[\frac{(\chi^2 - K_{yz}^2)}{K_{yy}} + K_{zz}\right]_{\sigma}. \tag{1b}$$

Here σ is the tracer mole fraction, χ the stream function, and $\mathbf{K}$ a mixing tensor along (y,z), the meridional and vertical directions, respectively. Brackets denote the global average on an isopleth and Z^* (= 7·ln(1000/p) (km), p=isopleth pressure (mb)) is the isopleth pressure altitude at a specified reference latitude .

The data conform closely to this idealized model. Scatterplots of CO_2 [Boering et al. *this issue*] and CH_4 vs. N_2O were remarkably compact. Seasonal and interannual variations of CO_2 propagated uniformly upward from the troposphere (seasonal changes for CH_4 were undetectable when compared with earlier measurements [see Schauffler et al., 1993]). Hence we use Eq. (1) with data for CO_2, CH_4, and N_2O to derive mean rates for vertical transport in the stratosphere over the domain of the observations (15-60°N), analogous to early "eddy-diffusion" models [Lettau, 1951; Colegrove et al., 1965; Wofsy and McElroy, 1973; Hunten, 1975]. Here the CO_2/CH_4-N_2O coordinate system eliminates effects of variance due to reversible displacements of the tracer fields [Ehhalt et al., 1983], allowing us to exploit these displacements to infer tracer distributions above flight altitudes.

Mean K(Z*) for 1992-93

We derive K(Z*) by integrating the continuity equation,

$$\frac{\partial C}{\partial t} - \frac{1}{p}\frac{\partial}{\partial Z^*}\left[K(Z^*)\,p\frac{\partial C}{\partial Z^*}\right] = 0, \tag{2}$$

$$K(Z^*) = \left[p\frac{dC}{dN_2O}\frac{dN_2O}{dZ^*}\right]^{-1}_{z=z^*} \times \tag{3}$$

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$$p\left[\int_{N_2O(Z^*)}^{N_2O(Z^*_{top})} \frac{\partial C(N_2O(Z^*))}{\partial t} dN_2O \frac{dZ^*}{dN_2O} + \frac{\partial C(Z^*_{top})}{\partial t} H\right] .$$

Here $C = CH_4 + CO_2$, and the last term (with H≈6 km) approximates the flux at $Z^*=Z^*_{top}$. Eq. 3 was evaluated using data for $\Delta CO_2/\Delta N_2O$ and $\Delta CO_2(N_2O)/\Delta t$ [Fig. 2, Boering et al.,*this issue*], and $\Delta CH_4/\Delta N_2O$ = 0.0043 ppm/ppb. A profile for $N_2O(Z^*)$ was adopted from data for 24±4° (Fig. 1b), the reference latitude chosen to approximate global mean photolysis rates for N_2O. The profile for $N_2O(Z^*)$ from Fig. 1b was used to derive $K(Z^*)$ for 42 > Z* > 30 km, the interval with 70% of the N_2O gradient, using Eq. 3 with $\partial C(N_2O(Z^*))/\partial t$ replaced by Λ from Eq. (4) below. Including CH_4 increases vertical gradients by ~15%, with little effect on time derivatives, hence, neglect of CO_2 from CH_4 oxidation would give $K(Z^*)$ about 15% too large.

Profiles of $K(Z^*)$ (Fig. 1a) show a bottleneck just above the tropopause, implied by slow propagation of the seasonal oscillation. The fall minima and spring maxima for CO_2 require 4-7 months to propagate 2-3 km, i.e. from the tropopause to N_2O≈300 ppb. The bottleneck was inferred also in early studies of transport of heat, nuclear bomb debris, CH_4 and N_2O [e.g. Holton, 1986; Wofsy and McElroy, 1973; Hunten, 1975], from steep gradients observed just above the tropopause. The increase of $K(Z^*)$ above the tropopause in winter is implied by the rise in CO_2 for N_2O < 200 ppb; very slow vertical exchange at these levels is indicated in summer by virtually unchanged CO_2 from May to November.

The composite profile adopted for N_2O is not constrained to be consistent with the CO_2-N_2O relationships in SPADE. Figure 2a shows consistent solutions for $CO_2(Z^*)$ from Eq. (2) and for N_2O from

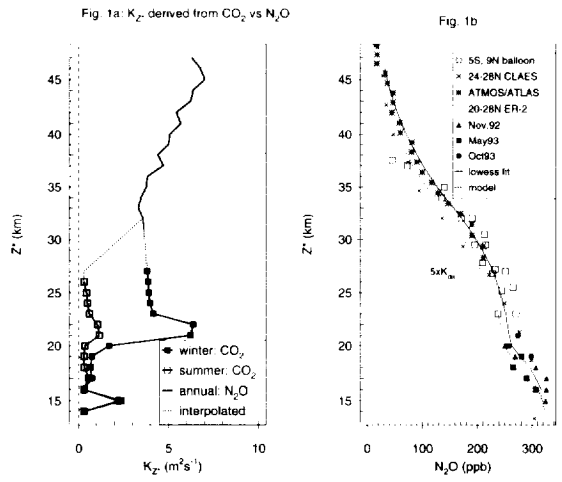

Figure 1a. Vertical profiles of $K(Z^*)$: summer (open □) and winter (filled □) using Eq. 3 and data for CO_2, CH_4, and N_2O (Z^*<26 km); solid line, using satellite data for $N_2O(Z^*)$ (Z^* > 30 km); dotted line, interpolated values.

Figure 1b. Vertical profile of N_2O for 15-25N. The line is a fit (locally-weighted least squares, "lowess") to data: Z^* >30 km, satellite observations November, 1992 [CLAES/UARS, A. Roche and J. Mergenthaler, private communication, 1994; ATMOS/ATLAS, M. Gunson, private communication, 1994]; 30 > Z* > 20 km, tropical balloon data [Goldan et al., 1981]; Z* < 20 km, ER-2, 20-28N, on dates indicated. Dotted lines show N_2O computed from the 1-D model, using $K(Z^*)$ from Eq. (3) and with 0.5× this value("0.5×K_{dir}").

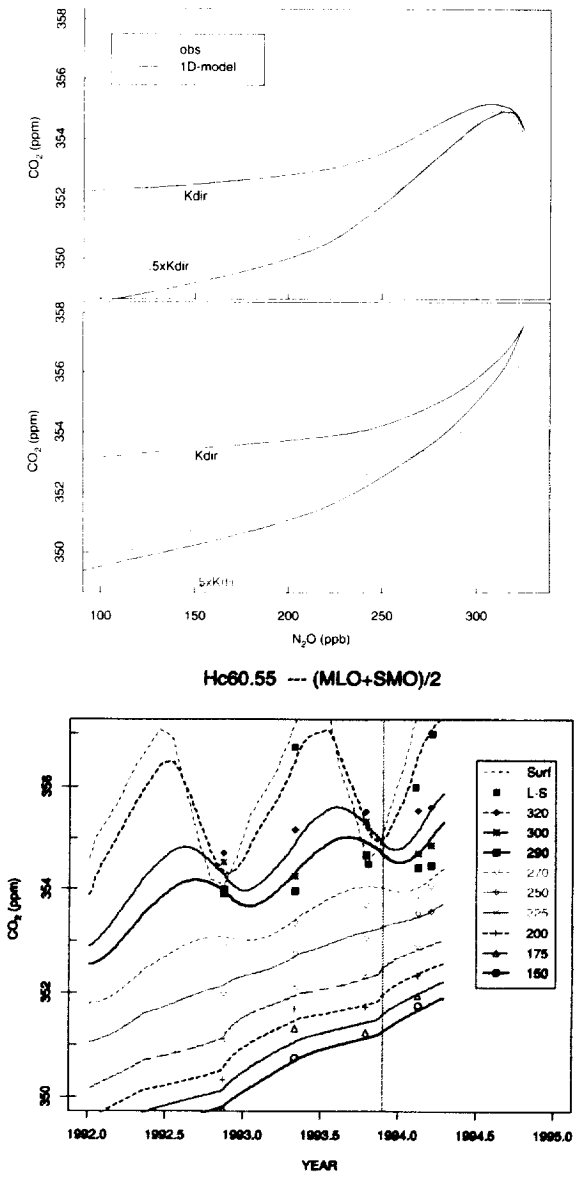

Figure 2a. Relationships for CO_2 vs N_2O computed using the 1-D model, with $K(Z^*)$ from Fig. 1a (≡K_{dir}), and scaled by 0.5, for November 1992 (upper) and May 1993 (lower).

Figure 2b. Concentrations of CO_2 for given N_2O from the 1-D model with $K(Z^*)=0.55*K_{dir}$ (lines), compared to observations (symbols). Data for CO_2 at the lowest altitude unambiguously above the tropopause (□ "L-S") [Boering et al, *this issue*] and the boundary condition for the 1-D model (---, "Surf", mean of NOAA/CMDL data at Samoa and Mauna Loa [T. Conway, private communication, 1994] delayed by 1 month) are also shown.

$$\frac{\partial N_2O}{\partial t} - \frac{1}{p}\frac{\partial}{\partial Z^*}\left[K(Z^*)p\frac{\partial N_2O}{\partial Z^*}\right] = \Lambda \cdot N_2O \ . \qquad (4)$$

Here we set tropospheric N_2O to 325 ppb, as given by the ER-2 ATLAS instrument. We set CO_2 at the bottom boundary to the mean of surface data from Mauna Loa and Samoa [T. Conway, private communication, 1994], delayed by one month to allow for tropospheric mixing, which approximates CO_2 observations just above the tropopause (Fig. 2b). In Eq. (4), $\Lambda = J_{N_2O} + k_5[O(^1D)]$ for 15N at equinox, J_{N_2O} is the photolysis rate (sec^{-1}), and k_5 is the rate constant for

$$O(^1D) + N_2O \rightarrow 2\,NO \quad (5a)$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2\,. \quad (5b)$$

The calculation commenced in 1982. The initial CO_2-N_2O relationship was specified by subtracting 15 ppm CO_2 (the global mean increase in the decade) from the observations for November 1992. Winter and summer profiles for $K(Z^*)_{dir}$ (Fig. 1a), or $0.5\times K(Z^*)_{dir}$, were repeated each year.

Observed CO_2-N_2O relationships are bracketed by models using $1\times$ and $0.5\times K(Z^*)_{dir}$ (Fig. 2a). The 1-D model simulates observed propagation of the CO_2 signal through the lower stratosphere remarkably well (using N_2O as the vertical coordinate), with the best fit for $K(Z^*)=0.55\times K(Z^*)_{dir}$ (Fig. 2b), and it projects changes observed in early 1994. Details of N_2O-CO_2 variations near the tropopause ($290<N_2O<325$ ppb) are not clearly delineated: these data were obtained on ascent and descent, adversely affecting the diode laser spectrometer.

Values of N_2O are somewhat lower than observed for the profile of $K(Z^*)$ giving the best fit to CO_2-N_2O data (Fig. 1b). This difference likely reflects errors in the specified vertical profile for N_2O, leading to an inaccurate global mean vertical flux of N_2O. The discrepancy contributes uncertainty to estimates of the rate of upward spread of HSCT exhaust; it could be resolved by extending measurements of CO_2, CH_4, and N_2O to the middle stratosphere.

A recent 3-D model [Hall and Prather, 1993] simulated the mean difference between stratospheric and tropospheric CO_2, however, CO_2 evolved uniformly vs N_2O through the year, lacking the observed seasonal asymmetry. The model gave qualitatively correct gradients near the tropopause, but finer vertical resolution (≈0.5 km, vs 3 km in the model) is needed for detailed comparison.

NO_y from stratospheric aviation

The concentration of NO_y was computed by solving

$$\frac{\partial NO_y}{\partial t} - \frac{1}{p}\frac{\partial}{\partial Z^*}pK(Z^*)\frac{\partial NO_y}{\partial Z^*} = P(N_2O(Z^*)) - \beta(NO_y)^2 \quad (6)$$

where $P(N_2O(Z^*))$ denotes production of odd nitrogen by (5a) or by aircraft, and $\beta(NO_y)^2$ is the sink for NO_y,

$$NO + h\nu \rightarrow N + O \quad (7a)$$

$$N + O_2 \rightarrow NO + O \quad (7b)$$

$$N + NO \rightarrow N_2 + O \quad (7c)$$

averaged along an N_2O isopleth. Solutions to (6) reproduce observed correlations for N_2O-NO_y (Figure 3a) [e.g., Loewenstein et al., 1993], virtually independent of $K(Z^*)$.

Figure 3b shows computed springtime perturbations to NO_y produced by hypothetical HSCTs injecting NO_y at $Z^*=20$ km for 10 years at a rate of 1.45×10^8 $cm^{-2}s^{-1}$, 60% of total fleet emissions for the Mach 2.4/EI 15 fleet scenario [Baughcum et al., 1993] (to approximate northern hemisphere cruise-level inputs). Each summer, excess NO_y accumulated near 20 km, then spread to higher altitudes, or was removed to the troposphere, in winter. The maximum ΔNO_y for the best-fit profile ($0.5\times K(Z^*)_{dir}$) was ≈7 ppb (Fig. 3b), 60% larger than predicted by most 2-D models. Values for ΔNO_y are insensitive to $K(Z^*)$ above, and proportional to $K(Z^*)$ below, the injection altitude (see curve for $1\times K(Z^*)_{dir}$, Fig. 3b). The perturbation is reduced by 50% for injection just 2 km lower (at $Z^*= 18$ km).

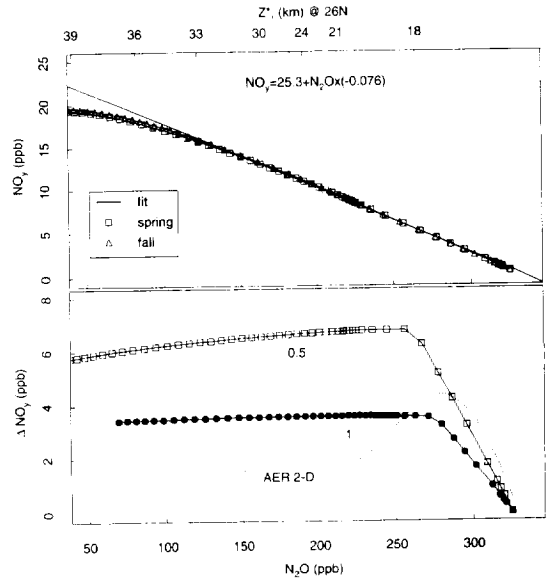

Figure 3a. N_2O-NO_y relationship computed from Eq. (6) and a linear regression for $N_2O>120$ ppb, $NO_y = 25.3 - 0.076\cdot N_2O$.

Figure 3b. ΔNO_y for HSCTs from the 1-D model for $K(Z^*)_{dir}$ (from Fig. 1a) and $0.5\times K(Z^*)_{dir}$, assuming injection at $Z^* = 20$ km of 60% of the fleet emissions for the nominal Mach 2.4/EI 15 scenario of Baughcum et al. [1993] (approximating northern hemisphere input at cruise). Results are shown from the AER 2-D model [Ko and Douglass, 1993] for the full scenario, averaged over the Northern hemisphere.

At altitudes higher than injection, ΔNO_y in 2-D models is smaller than in 1-D models, because exhaust does not spread uniformly along N_2O isopleths, giving rise to a local maximum in flight corridors. It is presently not clear if the 1-D model represents a global mean, as envision by Plumb and Ko [1992], or if the tropics represent a distinct regime essentially uncoupled from midlatitudes. Data for CO_2, CH_4, N_2O and NO_y are presently scarce or nonexistent for altitudes above 20 km, preventing confident prediction of ΔNO_y above flight levels; this is highly significant due to the enhanced reactivity of NO_x at high altitudes.

Conclusions

Temporal variations of tropospheric CO_2, relative to N_2O and CH_4, provide a unique signal for determining rates for transport in the lower and middle stratosphere. Seasonally-resolved data for CO_2, N_2O and NO_y are needed above 20 km to define rates for vertical advection and quasi-isentropic mixing, and fine-scale data near the tropopause are needed to define rates for transport in the key "bottleneck" region. Interannual variations, rates for interhemispheric exchange, and possible effects of the quasi-biennial oscillation need to be investigated. The present analysis shows that systematic tracer measurements over a period of years promise to help resolve these issues, providing essential constraints on models used to predict impacts of future HSCTs.

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